

bromobenzene (1)-benzene (2), water (1)-dimethyl sulfoxide (2), acetophenone (1)-toluene (2), acetophenone (1)-chlorobenzene (2), and benzene (1)-acetophenone (2). For the remaining mixtures we obtained positive values for A_{12} . However, for bromobenzene (1)-chlorobenzene (2) mixtures, the excess-volume parameter, A_{12} , was negligibly small. In the data of Sumer et al. (7), the values of A_{12} for toluene (1)-benzene (2) were ~5 times larger than in our systems. Further, they also studied the dependence of A_{12} on temperature, and it was found to be decreasing with increasing temperature for all of their systems. (A study along these lines is in progress for our systems.) The magnitudes of the parameters A_{12} and B_{12} depend strongly on the nature of reacting groups. Similar observations were made by several earlier workers (8-10).

Conclusions

Both refractive indexes and densities were measured for 10 carefully selected binary systems. The properties such as excess volume and excess polarizability of mixing were studied. Obviously, it seems to be quite clear that both of the parameters A_{12} and B_{12} are necessary to get a better insight into the structure of liquid mixtures. Obviously, data on more systems containing different chemical groups are needed to arrive at definite conclusions.

Acknowledgment

Part of the experimental work of this study has been carried out at The University of Texas at Austin and later completed at the Karnatak University, Dharwad, India. T.M.A. is highly grateful to Professor Petr Munk of The University of Texas for suggesting the topic of this research and providing the necessary facilities to carry out some of these experiments in his laboratory.

Literature Cited

- (1) Aminabhavi, T. M. Ph.D. Dissertation, The University of Texas, Austin, TX, 1979.
- (2) Aminabhavi, T. M.; Patel, R. C.; Jayadevappa, E. S.; Prasad, B. R. *J. Chem. Eng. Data*, submitted.
- (3) Aminabhavi, T. M.; Patel, R. C.; Bridger, K.; Jayadevappa, E. S.; Prasad, B. R. *J. Chem. Eng. Data*, submitted.
- (4) Aminabhavi, T. M.; Munk, P. *Macromolecules* 1979, 12, 1186.
- (5) Aminabhavi, T. M. *J. Chem. Educ.*, in press.
- (6) Aminabhavi, T. M.; Munk, P. *Macromolecules* 1979, 12, 607.
- (7) Sumer, K. M.; Thompson, A. R. *J. Chem. Eng. Data* 1968, 13, 30.
- (8) Letcher, T. M.; Bayles, J. W. *J. Chem. Eng. Data* 1971, 16, 266.
- (9) Rowlinson, J. S. "Liquids and Liquid Mixtures", 2nd ed.; Butterworth: New York, 1969.
- (10) Hicks, C. P.; Young, C. L. *Chem. Rev.* 1975, 75, 119.
- (11) All of the literature values for pure solvents were compiled from: Weast, R. C., Ed.; "Handbook of Chemistry and Physics", 58th ed.; CRC Press: Boca Raton, FL, 1977-78.

Received for review March 23, 1981. Accepted August 3, 1981.

Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 2. Binary Mixtures of 1,3-Dioxolane with Toluene

Romolo Francesconi, Fabio Comelli,[†] and Carlo Castellari*

Istituto Ciamician, Università di Bologna, 40126 Bologna, Italy

Vapor-liquid equilibrium data of binary mixtures of 1,3-dioxolane with toluene were obtained with a Stage-Müller apparatus at pressures of 150, 300, 500, 650, and 740 mmHg. The values of the activity coefficients were correlated by means of the Wilson expression, whose parameters show a marked dependence on the temperature. The values of the activity coefficients lead to the conclusion that the system is nearly ideal in the liquid phase.

In two previous papers (1, 2) we have studied the vapor-liquid equilibria of the following systems: (a) 1,3-dioxolane-water (1); (b) 1,3-dioxolane-*trans*-1,2-dichloroethylene (2); (c) 1,3-dioxolane-trichloroethylene (2); (d) 1,3-dioxolane-tetrachloroethylene (2). The values of the liquid-phase activity coefficients, evaluated from the experimental data, show that system a is strongly nonideal, systems b and c are almost ideal, and system d is appreciably nonideal.

In this paper we extend our study to the system 1,3-dioxolane-toluene. The vapor-liquid experimental data are

correlated by means of the Wilson equation.

Experimental Section

1,3-Dioxolane (Fluka product, analytical grade, 99%) was purified following the procedure given in ref 1. The toluene (Carlo Erba RPE product) was used without purification. The vapor-liquid measurements were carried out with a Stage-Müller apparatus, described elsewhere (4), at $P = 150, 300, 500, 650,$ and 740 mmHg.

Table I and Figure 1 collect the experimental $t-x_1-y_1$ values (where t is the temperature and x_1 and y_1 are the mole fractions in the liquid and vapor phases, respectively). The values of x_1 and y_1 were determined with an Abbe refractometer; the refractive index-composition data of the system 1,3-dioxolane-toluene are reported in Table II. The experimental errors for the measured properties P , t , x_1 , and y_1 are 2 mmHg, 0.1 °C, 0.2%, and 0.2%, respectively. The literature refractive index of toluene is $n_D^{25} = 1.4941$ (3); the toluene molar volume is obtained from the density of the pure component at 20 °C (3). The vapor pressures of the pure toluene and 1,3-dioxolane are expressed by the usual relation $\log P^0 = A + B/T$ (P^0 in mmHg) obtained from the vapor-liquid data of this work with a least-squares method. For the component toluene $A = 7.711$ and $B = -1851.1$, whereas for

[†] Centro di Studio per la Fisica delle macromolecole del CNR, 40126 Bologna, Italy

Table I. t - x - y Data for 1,3-Dioxolane-Toluene

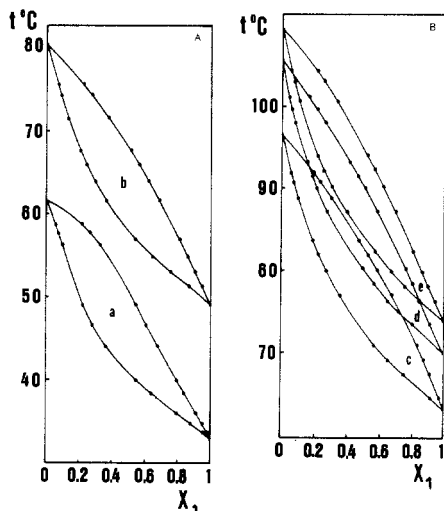
$P = 740$ mmHg			$P = 650$ mmHg			$P = 500$ mmHg			$P = 300$ mmHg			$P = 150$ mmHg		
$t/^\circ\text{C}$	x_1	y_1	$t/^\circ\text{C}$	x_1	y_1	$t/^\circ\text{C}$	x_1	y_1	$t/^\circ\text{C}$	x_1	y_1	$t/^\circ\text{C}$	x_1	y_1
73.9	1.000	1.000	69.9	1.000	1.000	62.4	1.000	1.000	48.9	1.000	1.000	32.4	1.000	1.000
76.3	0.848	0.948	73.5	0.809	0.912	64.3	0.908	0.965	51.2	0.867	0.946	33.7	0.953	0.978
78.2	0.767	0.902	76.2	0.660	0.858	67.1	0.747	0.910	52.9	0.754	0.901	34.7	0.872	0.947
79.8	0.681	0.867	78.3	0.568	0.817	68.8	0.654	0.870	54.8	0.647	0.855	36.0	0.787	0.912
82.3	0.576	0.817	80.2	0.505	0.770	70.6	0.566	0.835	56.9	0.538	0.816	38.4	0.635	0.835
87.1	0.400	0.705	87.1	0.282	0.592	76.7	0.359	0.675	61.6	0.360	0.648	39.9	0.545	0.790
90.2	0.311	0.630	89.9	0.218	0.521	79.7	0.275	0.586	63.9	0.290	0.621	44.0	0.359	0.681
92.1	0.259	0.572	91.4	0.191	0.483	81.7	0.225	0.537	65.9	0.241	0.567	46.6	0.279	0.605
93.9	0.221	0.531	93.0	0.157	0.428	83.4	0.195	0.475	67.7	0.200	0.510	49.9	0.221	0.545
100.5	0.108	0.339	97.7	0.086	0.269	88.5	0.102	0.305	71.6	0.125	0.375	56.3	0.097	0.325
102.9	0.072	0.252	99.4	0.060	0.219	90.4	0.078	0.239	74.3	0.086	0.270	57.7	0.074	0.265
104.2	0.056	0.225	100.8	0.044	0.172	91.5	0.057	0.195	75.6	0.066	0.226	58.7	0.056	0.221
109.1	0.000	0.000	105.3	0.000	0.000	96.3	0.000	0.000	80.4	0.000	0.000	61.6	0.000	0.000

Table II. Refractive Index-Composition Data for 1,3-Dioxolane-Toluene

x_1	n_D^{25}	x_1	n_D^{25}
0.0000	1.4936	0.5634	1.4506
0.0624	1.4901	0.7014	1.4359
0.2391	1.4781	0.8214	1.4218
0.2965	1.4737	0.9628	1.4026
0.3896	1.4633	1.0000	1.3972

Table III. Values of the Parameters λ_{12} and λ_{21} in the Wilson Equation (Eq 1) at Various Pressures for 1,3-Dioxolane-Toluene

P/mmHg	$\lambda_{12}/(\text{J/mol})$	$\lambda_{21}/(\text{J/mol})$	σ/mmHg
150	1045.3 ± 128	-339.8 ± 150	5.0
300	1268.6 ± 6	-311.2 ± 6	1.3
500	1688.5 ± 62	-893.9 ± 59	2.5
650	2166.4 ± 47	-1255.5 ± 39	2.6
740	2316.7 ± 41	-1364.0 ± 33	2.5

Figure 1. t - x_1 - y_1 values for mixtures of 1,3-dioxolane-toluene at (a) 150, (b) 300, (c) 500, (d) 650, and (e) 740 mmHg.

1,3-dioxolane $A = 7.9456$ and $B = 1761$ (1).

The activity-coefficient data satisfied the semintegral consistency criterion which was used earlier for other binary mixtures with 1,3-dioxolane (4, 5). Within the limits of the experimental errors, the data obeyed this criterion with the assumption of no association between the components in the vapor phase. In fact, the integrals of the Gibbs-Duhem equation calculated for x_1 intervals of 0.1 never exceeded the error of the integral itself. The values of the activity coefficients γ_1 and γ_2 were correlated by means of the Wilson equation

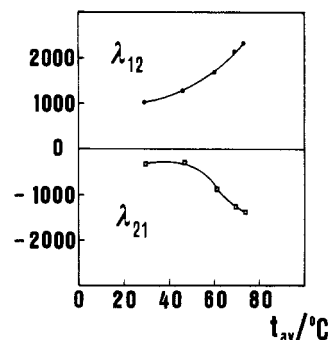
in $\gamma_k =$

$$-\ln(x_k + \Lambda_{kj}x_j) + x_j\{\Lambda_{kj}/(x_k + \Lambda_{kj}x_j) - \Lambda_{jk}/(x_j + \Lambda_{jk}x_k)\} \quad (1)$$

$$\Lambda_{kj} = v_j/v_k \exp(-\lambda_{kj}/RT) \quad k = 1,2; k \neq j \quad (2)$$

with the parameters λ_{kj} obtained with the least-squares procedure utilizing the objective function

$$\varphi = \sum_{r=1}^N [P - \sum_{k=1}^2 P_k^0(r) x_k(r) \gamma_k(r)]^2 \quad (3)$$

Figure 2. Values of the parameters λ_{12} and λ_{21} of the Wilson equation as functions of the average temperature in the isobaric group of the vapor-liquid data for the binary mixtures of 1,3-dioxolane-toluene.

where N is the number of the experimental data in each isobaric set and the γ_k 's are given by the Wilson equation (eq 1). Table III reports the parameters λ_{12} and λ_{21} together with their estimated standard errors and the root-mean-square deviation, σ , evaluated at the minimum of the objective equation 3. In Figure 2 are reported the values of the parameters λ_{12} and λ_{21} as functions of the average values of the temperature in each isobaric set of the experimental data.

The values of the activity coefficients lead to the conclusion that the binary mixtures of 1,3-dioxolane with toluene are nearly ideal in the liquid phase. In fact, the γ_k 's, calculated from the Wilson equation (eq 1) with the parameters λ_{12} and λ_{21} given in Table III, range from 1 to 1.3. Finally, the parameters λ_{12} and λ_{21} are strongly dependent on the average temperature of each isobaric set.

Literature Cited

- (1) Francesconi, R.; Castellari, C.; Arcelli, A.; Comelli, F. *Can. J. Chem. Eng.* **1980**, *58*, 113.
- (2) Comelli, F.; Castellari, C.; Francesconi, R. *J. Chem. Eng. Data*, in press.
- (3) Dreisbach, R. R. *Adv. Chem. Ser.* **1955**, No. 15, 12.
- (4) Francesconi, R.; Trevisoli, C. *Chem. Eng. Sci.* **1971**, *26*, 1331.
- (5) Francesconi, R.; Cojutti, A. *Chem. Eng. Sci.* **1971**, *26*, 1341.